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Chemistry of Urea Nitro Derivatives: II.* Synthesis of Nitramide from *N,N′*-Dinitrourea. New Reactions of Nitramide

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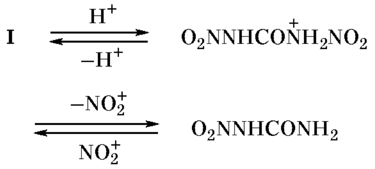
Abstract—Study of the hydrolysis of *N,N′*-dinitrourea resulted in the development of convenient procedures for synthesizing nitramide on the basis of urea. New reactions of nitramide were examined.

Nitramide NH_2NO_2, which was synthesized more than 100 years ago [2], still attracts researchers' attention as a simplest reactive starting compound for preparation of new structures, as the first member of the nitramine homologous series, as starting compound for synthesis of dinitramide, etc. Unfortunately, all known procedures for synthesis of nitramide are fairly complex, and they cannot ensure large-scale preparation of this product.

Our previous study [1] on the synthesis of *N,N′*-dinitrourea (**I**) and its properties showed that it readily undergoes hydrolysis with formation of nitramide (**II**):

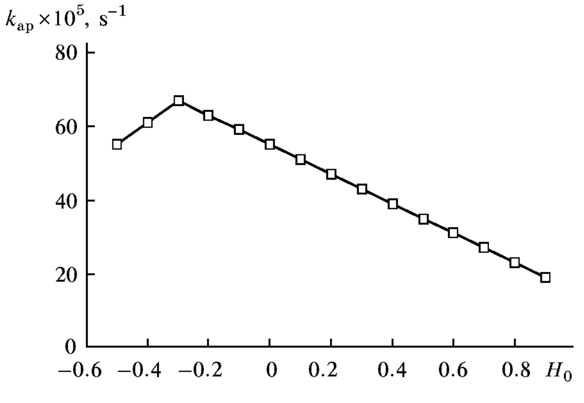
$$\underset{\textbf{I}}{(O_2NNH)_2CO} + H_2O \longrightarrow \underset{\textbf{II}}{2H_2N{-}NO_2}$$

Nitramide is formed almost quantitatively in the reaction of dinitrourea **I** with an equimolar amount of water. However, pure dinitrourea **I** is a highly reactive compound, which is extremely sensitive to mechanical disturbance, so that work with this substance is difficult and hazardous. Therefore, it was necessary to develop a convenient preparative procedure for synthesis of nitramide. Study of the kinetics of hydrolysis of dinitrourea **I** in water (c_0 = 0.1 M) showed that the apparent rate constant k_{ap} calculated on the assumption of first order of the reaction depends on the current dinitrourea concentration. A possible reason may be considerable change of the acidity of the medium in the course of hydrolysis since dinitrourea is a strong acid. This was confirmed by the results of a series of experiments on hydrolysis of **I** in aqueous sulfuric acid. The k_{ap} values no longer changed in sulfuric acid solutions with a concentration greater than 0.05 N. Raising the medium acidity in the range of H_0 from 0.8 to –0.3 k_{ap} resulted in increase of k_{ap}, and further increase in H_0 led to reduction of k_{ap} (see figure). At a sulfuric acid concentration of more than 60%, the contribution of the denitration process becomes appreciable, and nitrourea can be isolated from the reaction mixture:



$$\textbf{I} \underset{-H^+}{\overset{H^+}{\rightleftarrows}} O_2NNHCO\overset{+}{N}H_2NO_2 \underset{NO_2^+}{\overset{-NO_2^+}{\rightleftarrows}} O_2NNHCONH_2$$

Comparison of our results with the pK_a value of dinitrourea **I** in water (0.13±0.05; determined by



Plot of the apparent rate constants for hydrolysis of *N,N′*-dinitrourea (**I**) versus acidity of the medium; 30°C.

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[*] For communication I, see [1].

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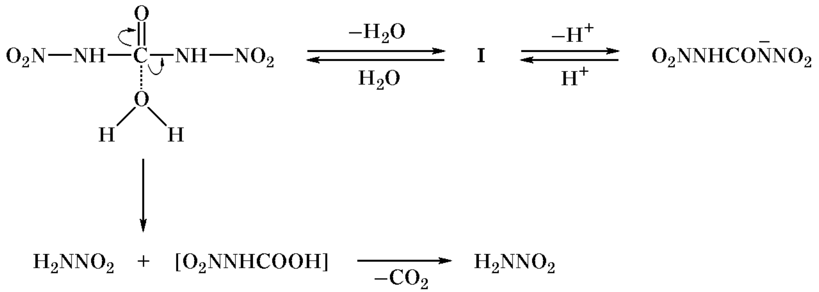
Scheme 1.



II

the procedure described in [3]) suggests that the reactive species in the hydrolysis is neutral molecule **I** (Scheme 1). Water is not the only nucleophile in this reaction. The formation of nitramide was also observed in anhydrous solvents, which may be explained by solvolysis.

No systematic studies of the salt effect were carried out. It was found that the rate of hydrolysis of dinitrourea in a 22% solution of ammonium nitrate is lower by a factor of 2.1–2.2 than in pure water. In going to a 40% solution of ammonium sulfate the rate of hydrolysis decreases 15-fold. Here, the main factor is likely to be ion exchange.

$$\underset{\mathbf{I}}{(O_2NNH)_2CO} + (NH_4)_2SO_4 \longrightarrow NH_4^+\ O_2NNHCO\bar{N}NO_2 + NH_4HSO_4$$

This reaction can be regarded as a convenient route to dinitrourea salts, which are poorly soluble in water and hence can readily be isolated.

Water-saturated solvents with small dielectric constants turned out to be attractive for carrying out the hydrolysis of dinitrourea due to the possibility for reducing its degree of dissociation and sufficient stability of nitramide in these media (see table).

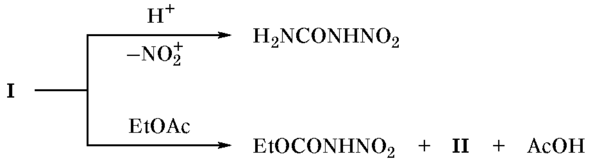
Apparent rate constants of the hydrolysis of *N*,*N*′-dinitrourea (**I**) at 30°C

Solvent	ε [4]	$[H_2O]$, %	$k_{ap} \times 10^5$, s^{-1}
1,4-Dioxane	2.2	4.9	34
Ethyl acetate	6.0	1.7	55
Ethyl acetate	6.0	3.3	62
Acetone	20.7	4.9	51
Methyl isobutyl ketone	13.7	1.9	39
Acetonitrile	36.2	4.9	50

Our results allowed us to develop several procedures for preparation of nitramide on the basis of extraction of compound **I** from aqueous solutions by water-immiscible solvents, followed by hydrolysis. As initial compounds we used urea, *N*,*N*′-dinitrourea (**I**), and salt **Ia** formed by urea and dinitrourea.

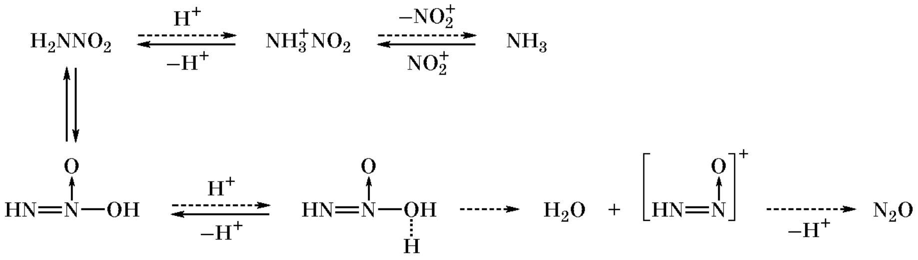
$$(NH_2)_2CO \xrightarrow{HNO_3/H_2SO_4} \mathbf{I} \xrightarrow{(NH_2)_2CO} \underset{\mathbf{Ia}}{(O_2NNH)_2CO\cdot(NH_2)_2CO}$$

Salt **Ia** is stable, weakly sensitive to shock, and poorly soluble in water; it is easy to store. In order to obtain nitramide from compound **Ia** it is sufficient to dissolve the latter in aqueous sulfuric acid, extract dinitrourea into ether, and subject it to hydrolysis. In any case the yield of nitramide is no less than 75%. The procedure for preparation of nitramide from urea without isolating intermediate products is the safest, but the product always contains small amounts of nitrourea and ethyl nitrocarbamate (which are formed from dinitrourea); these impurities can be removed only by reprecipitation and recrystallization.



Using salt **Ia** as starting compound, highly pure nitramide is obtained, which does not require additional purification. The product was identified by the IR spectra and chemical transformations, such as quantitative conversion into dinitramide by known procedure [5] and condensation with formaldehyde and ammonia to give dinitropentamethylenetetraamine whose yield exceeds that reported in [6].

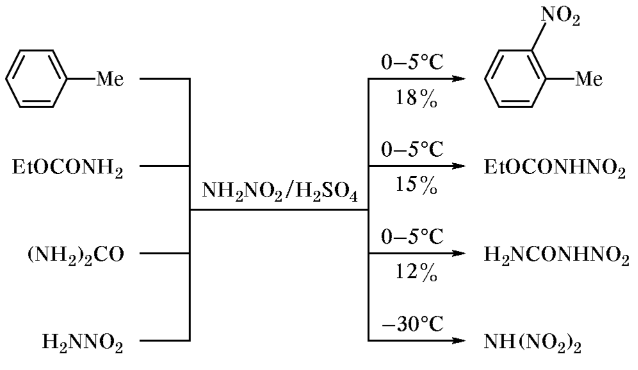
Scheme 2.



Having developed convenient methods for preparation of nitramide, we were able to focuse on some its reactions, primarily on decomposition in acid medium. The only identified products of nitramide decomposition in solutions of strong acids are nitrogen(I) oxide and water [2, 7], although denitration of nitramide in acid media was the subject of numerous studies.

$$H_2NNO_2 \xrightarrow{H^+} NH_3^+NO_2 \xrightarrow{H_2O} NH_4^+ + HNO_3$$

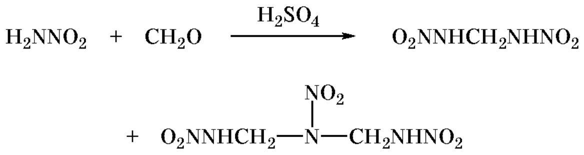
As early as 1895, Thiele and Lachman [2] reported on the possibility for formation of nitric acid in the course of decomposition of nitramide in acid medium. Hopkinson and Csizmadia [8] performed a theoretical analysis of the state of nitramide molecule protonated at the amino nitrogen atom; the authors revealed lengthening of the $\overset{+}{N}-N^{-}$ bond, which suggests its possible dissociation [8]. Nevertheless, even traces of nitric acid were not detected. We have considered possible ways of nitramide decomposition in acid medium (Scheme 2) and presumed that the reaction path leading to formation of nitric acid should be favored by addition of a substrate capable of reacting with nitric acid at a high rate. Such substrate may be toluene, ethyl carbamate, and nitramide itself. The reactions were carried out in concentrated sulfuric acid or in its mixture with sulfur(VI) oxide. We found that nitramide acts as nitrating agent.



In the course of decomposition of nitramide in concentrated sulfuric acid at 0–5°C we succeeded in detecting formation of up to 2.5% of nitric acid by spectrophotometry. Above 20°C, no nitric acid could be detected. We also failed to observe formation of nitric acid when the decomposition was performed in sulfuric acid with a concentration smaller that 90%. Taking into account the composition of the products, decomposition of nitramide in concentrated sulfuric acid can be illustrated by the following scheme:

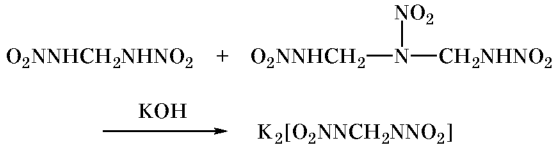
$$H_2NNO_2 + H_2SO_4 \longrightarrow N_2O + H_2O + HNO_3 + NH_4HSO_4$$

We also found that nitramide is quite stable in concentrated acids at low temperature. When nitramide was added to 94% sulfuric acid at –25 to –30°C, 20 min later the mixture contained up to 50% of the initial compound which is capable of being involved in various reactions. Nitramide readily reacts with formaldehyde in 90% sulfuric acid to give a mixture of products:



$$H_2NNO_2 + CH_2O \xrightarrow{H_2SO_4} O_2NNHCH_2NHNO_2 + O_2NNHCH_2\text{—}\overset{NO_2}{\overset{|}{N}}\text{—}CH_2NHNO_2$$

Treatment of the resulting nitramine mixture with potassium hydroxide in water leads to formation of 65% of methylenedinitramine dipotassium salt:

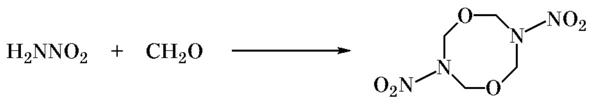


$$O_2NNHCH_2NHNO_2 + O_2NNHCH_2\text{—}\overset{NO_2}{\overset{|}{N}}\text{—}CH_2NHNO_2 \xrightarrow{KOH} K_2[O_2NNCH_2NNO_2]$$

In the presence of ethyl acetate at –5 to –8°C the yield of methylenedinitramine increases to 90%.

$$H_2NNO_2 + CH_2O \xrightarrow{H_2SO_4/EtOAc} O_2NNHCH_2NHNO_2$$

Alternatively, a solution of nitramide in ethyl acetate can be used. The other solvents are ineffective. The most important factor in the above reaction is the nitramide–formaldehyde ratio which should be (2.8–3.0) : 1. Raising the amount of formaldehyde leads to formation of 3,7-dinitro-1,5-dioxa-3,7-diazacyclooctane (dioxaoctogen):



At a nitramide–formaldehyde ratio of 1 : 2, dioxaoctogen is formed in more than 80% yield.

An interesting reaction was that between nitramide and acetic anhydride. Apart from decomposition, the formation of *N*-nitroacetamide was observed (yield 40%). Treatment of *N*-nitroacetamide with an alcoholic solution of potassium hydroxide gives a fairly stable salt:

$$H_2NNO_2 + Ac_2O \xrightarrow[-AcOH]{} AcNHNO_2$$

$$\xrightarrow[-H_2O]{KOH} Ac\bar{N}NO_2\ K^+$$

Acylation of nitramide with carboxylic acid anhydrides was not reported previously. This reaction opens one more way of utilizing nitramide in the synthesis of organic compounds.

EXPERIMENTAL

The IR spectra were recorded on a Specord M-80 instrument in KBr. The UV spectra were measured on Specord UV-Vis and Specord M-40 spectrometers in water.

Kinetic measurements. A sample of *N,N'*-dinitrourea was dissolved in appropriate medium to attain an initial concentration of 10 g/l. The solution was stirred using a magnetic stirrer, maintaining the temperature with an accuracy of ±0.1°C. When necessary, samples were withdrawn from the reaction mixture. They were diluted with water, and the concentration of dinitrourea was determined by spectrophotometry. The concentration of dinitrourea (c) in the reaction mixture was calculated by the equation $c = M D n/\varepsilon$, where M is the molecular weight of dinitrourea, D is the optical density, n is the dilution factor, and $\varepsilon = 13000\ \mathrm{l\,mol^{-1}\,cm^{-1}}$.

The apparent first-order rate constants were calculated using standard equation. Doubly distilled water, purified and freshly distilled organic solvents, and sulfuric acid of chemically pure grade were used in experiments; *N,N'*-dinitrourea was synthesized by the procedure described in [1].

Preparation of nitramide from urea. Oleum (20% of SO_3), 35 g, was added to 35 g of nitric acid (d = 1.5 g/cm^3), and 10 g (0.1667 mol) of urea was added in portions at –5 to 0°C under continuous stirring. The mixture was stirred for 40 min at 0 to 5°C and poured while stirring into 300 g of an ice–water mixture, maintaining the temperature below 10°C. The mixture was extracted with ethyl acetate (2 × 100 ml and 4 × 50 ml), and the extract was washed with water (3 × 40 ml), kept for 2 h at 20°C, and evaporated to dryness under reduced pressure. Yield 15.5 g (75%). The product was dissolved in 30 ml of ether, the solution was poured into 400 ml of hexane, and the precipitate was filtered off. Additional recrystallization from dichloroethane–2-propanol (9 : 1) gave 13 g (63%) of nitramide with mp 78°C. UV spectrum (H_2O): λ_{max} = 206 nm, $\varepsilon = 7600\ \mathrm{l\,mol^{-1}\,cm^{-1}}$.

Preparation of nitramide from dinitrourea. The nitration of urea was carried out as described above. After keeping for 40 min at 0–5°C, the mixture was cooled to –12°C, and the precipitate of dinitrourea was filtered off through a glass filter, washed with cold methylene chloride (3 × 10 ml), and squeezed. The product was dissolved in 300 ml of ether at 0°C under continuous stirring, and the solution was washed with water (2 × 20 ml), kept for 4.5 h at 20°C, and evaporated to dryness under reduced pressure. Yield 15 g (73%).

Preparation of nitramide from the urea salt of dinitrourea. Dinitrourea was synthesized following the above procedure. A 13.6-g (0.09-mol) portion of dinitrourea was added to a solution of 6.6 g (0.11 mol) of urea in 12 ml of water at a temperature not exceeding 20°C. The mixture was kept for 15 min and cooled to 5°C, and the precipitate was filtered off, washed with a small amount of ice water, and dried in air. Yield of salt **Ia** 15.45 g (90%), mp 91–95°C (decomp.). The resulting salt was added in small portions to a solution of 15 g of sulfuric acid in 35 ml of water, stirred at 20°C. When the mixture became homogeneous, it was extracted with ether (3 × 60 ml), and the extract was left to stand for 4 h at room temperature and was then evaporated to dryness under reduced pressure. Yield 8.24 g (90%), mp 83–84°C (Boetius device), 81–82°C (in a capillary), 79.7°C (DSC). UV spectrum (H_2O): λ_{max} = 206 nm, $\varepsilon = 7680\ \mathrm{l\,mol^{-1}\,cm^{-1}}$.

Hydrolysis of dinitrourea. Distilled water, 0.18 g (0.01 mol), was added to 1.5 g (0.01 mol) of dinitrourea prepared by the procedure desribed in [1]. The mixture was carefully stirred and was left to stand for 8 h at room temperature. Initially, a moderate gas evolution was observed. When the reaction was complete, we isolated 1.21 g (98%) of nitramide, mp 73°C. The product contained 99% of the main substance (no dinitrourea impurity was detected by spectrophotometry).

Decomposition of nitramide. Nitramide, 6.2 g (0.1 mol), was carefully added over a period of 30 min to 37 g of 94% sulfuric acid maintained at –5°C. The mixture was kept for 3 h at that temperature and poured into 100 ml of water. Spectrophotometric analysis revealed the presence of nitric acid, λ_{max} = 203 nm, ε = 9000 $l\,mol^{-1}\,cm^{-1}$, 0.16 g (2.5%). For comparison, we also analyzed by spectrophotometry a solution of 94% sulfuric acid and a solution of nitramide decomposition products in 80% H_2SO_4. No absorption was observed in the range 200–210 nm.

Preparation of dinitramide. Nitramide, 6.2 g (0.1 mol), was added in small portions to 33 g of oleum (20% of SO_3) at –30°C. After 10 min, a 1-ml portion of the mixture was withdrawn and poured into 25 ml of water; dinitramide was detected by spectrophotometry, λ_{max} = 285 nm, ε = 5670 $l\,mol^{-1}\,cm^{-1}$.

Nitration of urea. Nitramide, 18.6 g (0.3 mol), was added in portions over a period of 1 h to a solution of 6 g (0.1 mol) of urea in a mixture of 40 ml of 94% sulfuric acid and 10 ml of 30% oleum, maintained at –5°C. After 10 min (from the reaction start), nitrourea was detected by spectrophotometry, λ_{max} = 260 nm (pH 8). After 45 min, the mixture was poured into ice water, and the precipitate was filtered off. The filtrate was extracted with ethyl acetate (5 × 50 ml), and the precipitate was dissolved in the extract. The extract was washed with water, dried over $MgSO_4$, and evaporated to dryness. Yield of nitrourea 1.3 g (12%), mp 154–159°C (with decomposition).

Nitration of ethyl carbamate. Nitramide, 12.4 g (0.2 mol), was added in small portions at 0–5°C to a solution of 8.9 g (0.1 mol) of ethyl carbamate in 30 ml of 94% sulfuric acid. The mixture was kept for 30 min, poured into an ice–water mixture, and extracted with ether (5 × 50 ml). The extract was washed with water, dried over $MgSO_4$, and evaporated. Yield of ethyl *N*-nitrocarbamate 2 g, mp 61–62°C (published data [2]: mp 64°C).

Nitration of toluene. Nitramide, 18.6 g (0.3 mol), was added over a period of 1.5 h at –15 to –10°C to a solution of 9.2 g (0.1 mol) of toluene in 40 ml of 94% sulfuric acid, and the mixture was kept for 45 min at –5 to –2°C. It was then poured onto ice, and the oily substance was separated, washed with water, and kept under reduced pressure until constant refractive index. Yield of *o*-nitrotoluene 2.5 g (18%), n_D = 1.5448 [9].

Preparation of methylenedinitramine. A solution of 1.5 g (0.05 mol) of paraformaldehyde in 30 ml of 90% sulfuric acid was added at –10 to –8°C to a solution of 9.3 g (0.15 mol) of nitramide (98.8% purity) in 30 ml of ethyl acetate. The mixture was kept for 20 min at –8 to –5°C and poured into 100 ml of water. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (3 × 50 ml). The combined extracts were washed with water (2 × 40 ml), dried over magnesium sulfate, and evaporated to dryness under reduced pressure. The crystalline residue was evacuated for an additional 20 min. Yield 6.25 g (92%, calculated on the formaldehyde taken), mp 94–98°C. After recrystallization from dichloroethane, mp 102–104°C (published data [10]: mp 101°C).

Preparation of a mixture of methylenedinitramine and 1,3,5-trinitro-1,3,5-triazapentane. Nitramide, 3.31 g, was added in portions at –5°C to a solution of 0.6 g of paraformaldehyde in 20 ml of 90% sulfuric acid. The mixture was kept for 10 min at –5 to 0°C and poured into 50 ml of water containing ice. The precipitate was filtered off, washed with a small amount of cold methanol and with ether, and dried. Yield of 1,3,5-trinitro-1,3,5-triazapentane 0.5 g, mp 130–133°C (decomp.). After repeated treatment with ice-cold ether, the melting point rose to 153–154°C. IR spectrum, ν, cm^{-1}: 3360 (N–H); 3040, 2920 (CH_2); 1600, 1550 (NO_2). Found, %: C 10.8; H 3.0; N 39.8. $C_2H_6N_6O_6$. Calculated, %: C 11.42; H 2.85; N 40.0.

The filtrate was extracted with ethyl acetate (3 × 50 ml). The extract was washed with water, dried over magnesium sulfate, and evaporated under reduced pressure to obtain 1 g of methylenedinitramine with an impurity of 1,3,5-trinitro-1,3,5-triazapentane (a characteristic sharp peak at 3360 cm^{-1} in the IR spectrum), mp 104–109°C. By fractional crystallization from acetone–ether we isolated 0.3 g of 1,3,5-trinitro-1,3,5-triazapentane with mp 130–135°C. Evaporation of the organic phase under reduced pressure gave 0.6 g of methylenedinitramine, mp 102–104°C. The overall yield of the condensation products was 65%. The yield of purified 1,3,5-trinitro-1,3,5-triazapentane was 35%.

Preparation of 3,7-dinitro-1,5-dioxa-1,7-diazacyclooctane. To a solution of 3 g (0.1 mol) of paraformaldehyde in 18 ml of 90% sulfuric acid we added 15 ml of ethyl acetate and, at –12 to –10°C, 3.1 g (0.05 mol) of nitramide. The mixture was kept for 30 min at –10 to –5°C and poured into 60 ml of water containing ice. The solvent was evaporated under reduced pressure, and the precipitate was filtered off, washed with water, and dried. Yield 4.3 g (80%), mp 264–266°C (decomp., from acetone); published data [11]: mp 263–264°C.

Preparation of *N*-nitroacetamide. Nitramide, 1.86 g (0.03 mol), was dissolved at 18–20°C in 40 ml of acetic anhydride, and the solution was kept for 2 days. The solution was evaporated to dryness under reduced pressure at a temperature not exceeding 40°C. Yield 1.12 g (36%), mp 81–82.5°C; published data [12]: mp 79°C. Found, %: C 23.2; H 4.0; N 28.4. $C_2H_4N_2O_3$. Calculated, %: C 23.08; H 3.87; N 26.92.

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